2 of 3

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Quarterly Technical Summary
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Synthesis of New Fluorine Containing Compounds

OZARK-MAHONING COMPANY

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I. SUMMARY

Experimental work this quarter consisted of the following:

A. Continuation of work on solid-gas reactions.

B. Infrared analysis of products of previous experiments using a Perkin-Elmer IR-337 Spectrophotometer.

C. Salt fusions and electrolysis of molten salts.

The fusions have been carried out in a nickel crucible or glass tube. Electrolyses have been carried out in a stainless steel cell into which a nickel crucible containing the salts could be placed.

II. DISCUSSION

A. SOLID-GAS REACTIONS.

Cesium fluoride was allowed to react with nitrous oxide in an attempt to prepare the N_2OF^- ion. There was no reaction evident under the conditions utilized.

Cesium fluoride, when allowed to react with dinitrogen trioxide, gave a product that consisted of a mixture of cesium nitrate and cesium fluoride. The formation of the nitrate might be explained by assuming the dissociation of N_2O_3 into nitrogen dioxide and nitric oxide. Nitrogen dioxide, when in excess, was shown in the previous quarterly report to react with cesium fluoride to form cesium nitrate. Because it was only the solid phases that were of primary interest no attempt was made to ascertain the composition of the gaseous phase; however, it seems quite likely that nitrosyl fluoride is formed.

Fluorine was allowed to react with cesium nitrite at temperatures below ambient and pressures less than atmospheric. Cesium nitrite was converted to the fluoride in each case.

In the reaction of KSO_2F with NO_2, the product when treated with water gives off NO_2 and gives a strong sulfate test. It appears to be a complex mixture consisting of starting materials, KF and perhaps $NOSO_3F$. Because of the absence of N-F absorptions in the infrared spectra, it is felt that further work on this reaction is unwarranted.

B. INFRARED ANALYSES.

Infrared spectra of the solid products of all previous reactions have been made. These reactions are as follows:

a) cesium fluoride with nitric oxide, dinitrogen tetroxide, dinitrogen trioxide, nitrosyl fluoride, and nitryl fluoride.

b) cesium nitrate or nitrite (or the potassium salt) with fluorine.

c) NO_2 with KSO_2F.

None of the infrared spectra had any absorptions characteristic of a N-F bond. These are summarized in Table I.

C. SALT FUSIONS AND ELECTROLYSIS OF MOLTEN SALTS.

Since sodium monofluorophosphate can be prepared by a simple fusion of NaF and $NaPO_3$ it was felt that analogous fusions of nitrates, nitrites and hyponitrites should be attempted.

When a 1:1 mixture of $CsNO_3$ and cesium fluoride was heated, no constant melting point was observed although it did begin to melt around 250°. At about 390° it appeared to be boiling or at least some evolution of gases due to decomposition; however, the temperature continued to rise until 500° at which point it remained constant. At all times there appeared to be some solids suspended in the melt. On continued heating the crucible was severely attacked and the melt became almost black in color. This color must be attributed to oxides of nickel. Fluorine analysis showed no significant change in composition. When the mixture was fused in a glass tube the melt acquired a slightly violet color. Infrared spectra of this sample indicated the presence of $CsNO_2$ in the $CsNO_3$.

Cesium nitrite and cesium fluoride (1:1) mixtures were treated in the same manner. They began to melt around 320° although there was no constant melting point. Boiling or decomposition started at 588° and became constant at 625°. Again there was a dark color and heavy attack on the crucible. Infrared analysis of a sample melted in a glass tube indicated the presence of both the nitrate and nitrite.

No attempt was made to protect the melt from the atmosphere. Since both the nitrate and nitrite are present in the melt regardless whether the nitrate or the nitrite is the starting material, it appears that perhaps the presence of atmospheric oxygen is of significance. This would suggest some sort of a nitrate-nitrite equilibrium.

TABLE I

Reaction	Conditions, T & P	Infrared Analysis
$CsNO_3 + F_2$	300 mm to 80 atm. -60° to 100°	no N-F absorptions in any case.
$KNO_2 + F_2$	10 atm., 25°	no N-F absorption
$CsNO_2 + F_2$	300 mm, -40°	no N-F absorption
$CsF + NO_2$ (xs)	6 atm., 360°	Fluoride converted to the nitrate no N-F absorptions
$CsF + FNO$ (xs) or FNO_2 (xs)	25° and 150° P (not calc.)	Small amount of $CsNO_3$ present suggesting that the fluoride reacted with NO_2 present as impurity in FNO or FNO_2; no N-F absorptions.
$CsF + NO$ (xs)	560° P (not calc.)	Both $CsNO_2$ and $CsNO_3$ present; no N-F absorptions; no reaction occured otherwise.
$CsF + N_2O$ (xs)	100° and 300° P (43 and 65 atm.)	no reaction.
$CsF + N_2O_3$ (xs)	100° P (not calc.)	some NO_3^- present; no N-F absorptions.
$KBO_2F + NO_2$	25° P (not calc.)	complex mixture probably containing mostly KF and $NOSO_3F$. no N-F absorptions
$CsNO_2 + F_2$	300 mm -35 to -40°	some nitrite present no N-F

After a mixture of $Na_2N_2O_2$ and NaF was heated to about 500° a sample was analyzed by infrared. The spectra showed $NaNO_2$ and $NaNO_3$ to be present.

Very little can be said at this time about the products of electrolysis of $CsNO_3$ and CsF. Infrared spectra were obtained for the gaseous products. The spectra contained absorptions for only NO_2 and SiF_4; however, the gases were transferred in a glass vacuum manifold. The presence of NO_2 and SiF_4 strongly suggest the gas product was FNO. The infrared cell for gaseous samples is made of one inch Monel tubing using silver chloride windows affixed with Kel-F wax. The path length is 5 cm. The solid phase was highly contaminated with the corrosion products from the electrodes; hence, no conclusions can be made at this time.

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III. EXPERIMENTAL

A. SOLID-GAS REACTIONS:

These reactions were carried out in a 300 ml. Monel cylinder.

Nitrogen dioxide and KSO_2F (1:1 and 1:3 molar ratios) were placed in a cylinder and allowed to react at ambient temperature for several days. After the gases were discharged the solids were observed to have a pale green color, decomposed in water to give NO_2 and a strong SO_4 test. Analysis gave a F^- content of 15.75% and K- content of 34.15%.

Cesium fluoride and nitrous oxide (in excess) were placed in a cylinder and heated to 100° for 40 hours and to 300° for 24 hours. The CsF was recovered unchanged in each case.

Dinitrogen trioxide in excess and CsF were heated in a cylinder to 100° for 40 hours. After the gases were discharged a 6% weight gain was observed. Analysis gave F = 9.52% and Cs = 77.3%. Infrared spectra (KCl pellet) indicated the presence of NO_3^-.

Experiments were carried out in which $CsNO_3$ and $CsNO_2$ were allowed to react with fluorine at low temperatures and pressures. A cylinder with F_2 and cooled with liquid nitrogen was connected to another cylinder containing $CsNO_3$. The cylinder containing the salt was cooled to -110°, -80° or -40°. Reaction times varied from three to eight hours. After the reaction period the excess fluorine was pumped off and a gauge connected to the cylinder to monitor any pressure changes that might occur on warming the cylinder to room temperature. No pressure changes were observed. The cylinder was then checked for weight changes. The contents were then analyzed. At -110° there was a weight loss of 4%. Fluorine analysis was 0.34%.

In the nitrite experiment the following were observed:

T, °C	Weight change	%F
-110	none apparent	0.28
- 80	none	----
- 40	-2%	3.00

At temperatures below -40°there is little or no reaction. The product, if any, is cesium fluoride.

The salt fusions were made in a nickel crucible placed in a crucible furnace.

A cell for electrolysis of melts was constructed of stainless steel pipe sealed by welding a plate on one end and a flange welded on the other. The salt mixture was placed in a nickel crucible which in turn was placed in the cell. A plate, having two Swagelok fittings and a port for the electrode which was to be inserted in the melt, was bolted to the flange using a Teflon gasket. The nickel electrode was inserted through a Teflon collar which acted as a seal as well as an insulator for the cell which was used as the other electrode. The cell was then placed in a furnace. A nitrogen line was connected to one of the fittings and the other was connected to a copper cold trap. A coil of copper tubing through which water flowed was placed around the top of the cell to prevent decomposition of the Teflon gaskets. The cell was then heated to the desired temperature. Nitrogen was passed through the cell to dilute and sweep out the gaseous products formed to minimize the possibility of explosive mixtures accumulating. No attempt was made to isolate the gaseous products of the anode from those of the cathode. Electrolyses were made using a voltage of 6 to 10 volts and a current of 1 to 2 amperes.

When a melt of $CsNO_3$ and CsF(1:1) was electrolyzed at about 550°, both the nickel crucible and the electrode were severely attacked. The melt afterwards was almost black in color. Infrared analysis showed $CsNO_3$ and $CsNO_2$ present. Infrared analysis of the gaseous products showed NO_2 and SiF_4; however, the gases (presumably FNO) were handled in a glass manifold which would account for the SiF_4.

Because of the extensive corrosion of the nickel components, some attention is now being given to this problem. One possible solution to this may be gold-plating of the nickel.

IV. FUTURE WORK

1. High pressure reactions will be undertaken as soon as the remainder of equipment which has been ordered is received.
2. Work on electrolyses will continue as well as attempts to eliminate corrosion problems.
3. Conductivity equipment is being requisitioned.